Cadmium Alternative Coating Corrosion Performance on Steel; Non-Cr^{+6} Primer Considerations

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SERDP / ESTCP Sustainment Workshop,
26-28 February 2008, Tempe, AZ

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **FEB 2008**	2. REPORT TYPE	3. DATES COVERED **00-00-2008 to 00-00-2008**

4. TITLE AND SUBTITLE **Cadmium Alternative Coating Corrosion Performance on Steel; Non-Cr+6Primer Considerations**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Air Warfare Center - Aircraft Division,AIR 4.3.4,22347 Cedar Point Road,Patuxent River,MD,20670**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Surface Finishing and Repair Issues for Sustaining New Military Aircraft Workshop, February 26-28, 2008, Tempe, AZ. Sponsored by SERDP/ESTCP.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**47**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Outline

- NAVAIR Test Result Summary / HSS JTP Sec. 4
  - Acidified Salt Fog, ASTM G 85.A4
    - Bare Inorganic Coatings w/Cr^{+6} post
    - Primed/Painted (MIL-PRF-23377 Class C2 and N; MIL-PRF-85582-N (non-chromate inhibitors); Topcoat: MIL-PRF-85285 polyurethane
  - Fatigue (Air & 3.5% NaCl), SCC, Residual Stress
    - NACE Dec. 07 (E. Lee, et. al.)
- Cd Alts Comparisons / Conclusions
- Non-Cr Primer Demonstration Status

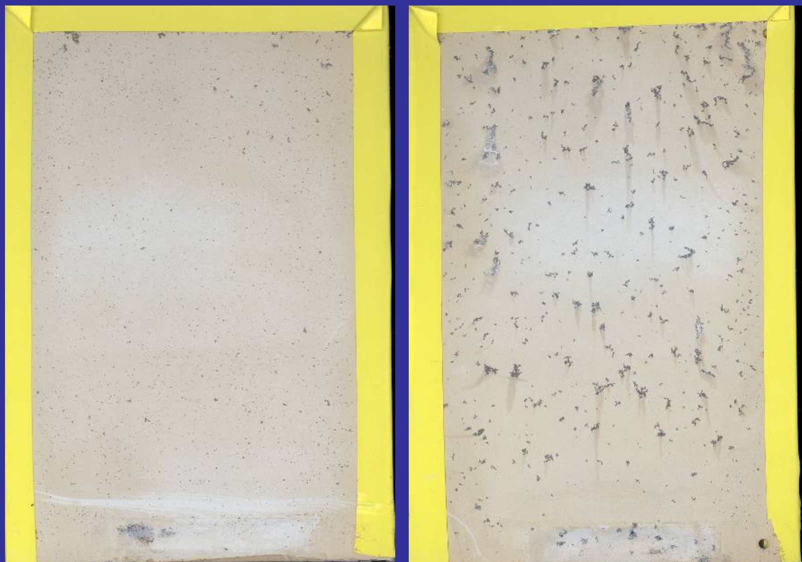
Sulfur Dioxide (SO_2) Acidified Corrosion Test Results, ASTM G 85, Annex 4

Tested panel images, duration:

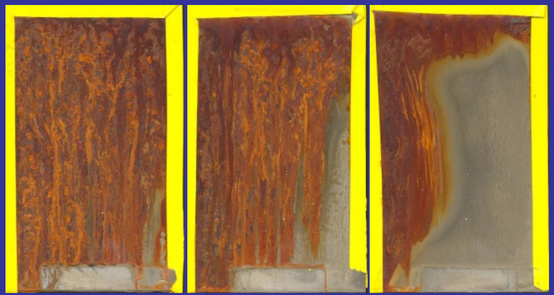
- 168 h (1 week)
- 500 h (3 weeks)
- 1000 h (6 weeks) - Painted

Corrosion Ratings: ASTM D 1654

Alumiplate, Unscribed – 500 hrs



Cadmium, Unscribed 168 hrs

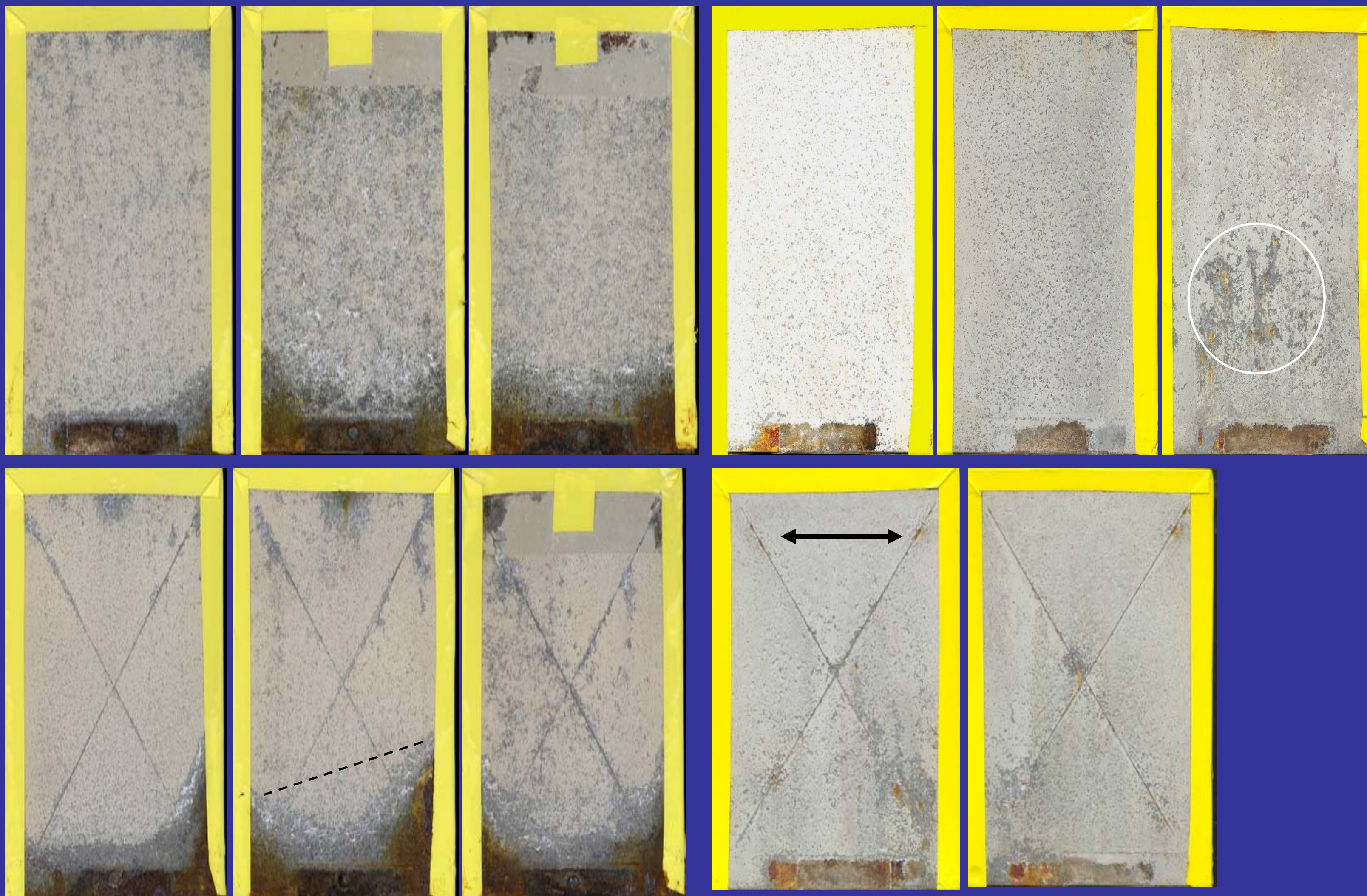


LHE Zn-Ni, Scribed – 168 hrs

Alumiplate, Scribed – 500 hrs

Sputtered Al, Unscribed – 500 h

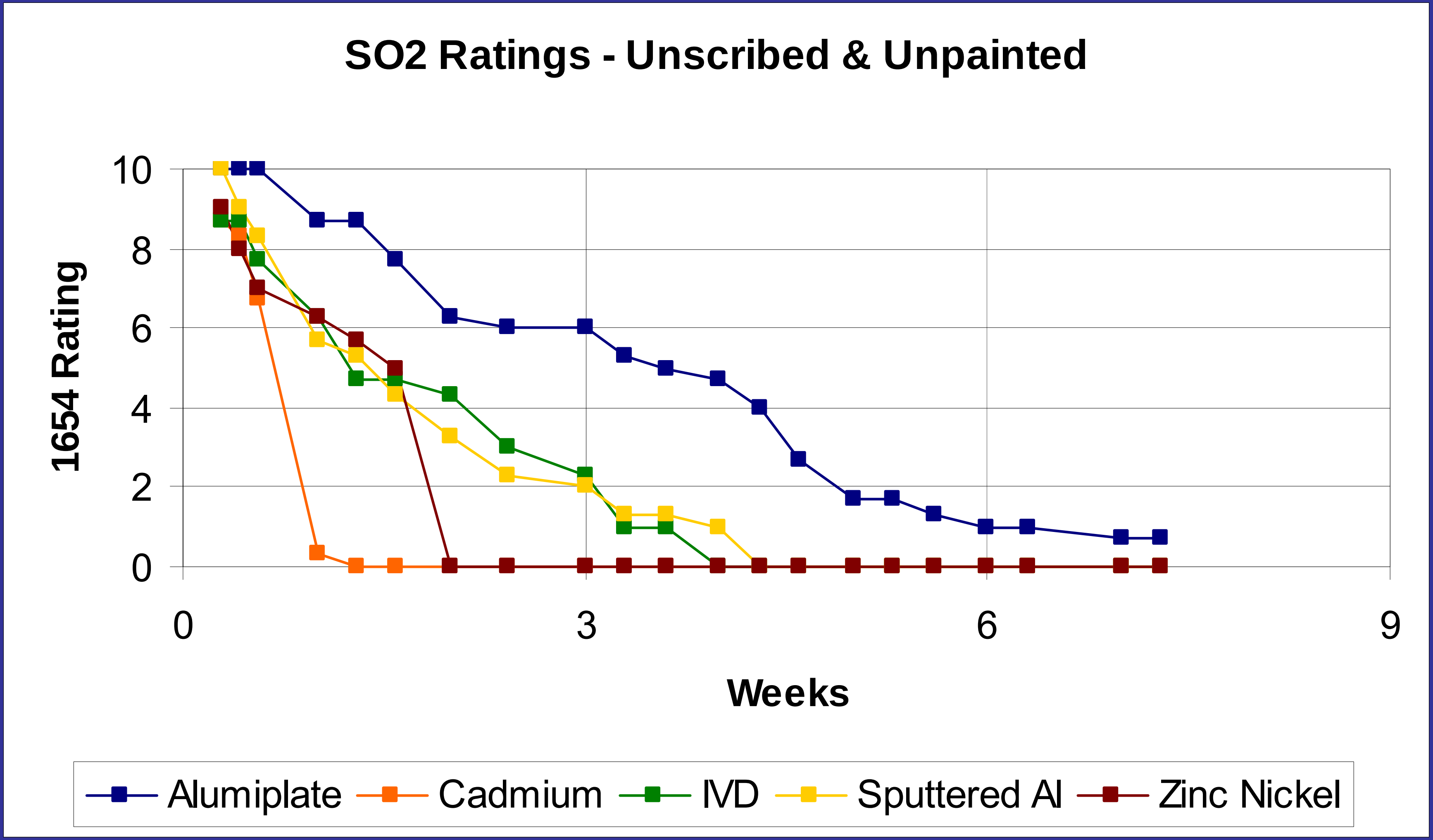
IVD-Al, Unscribed – 500 h



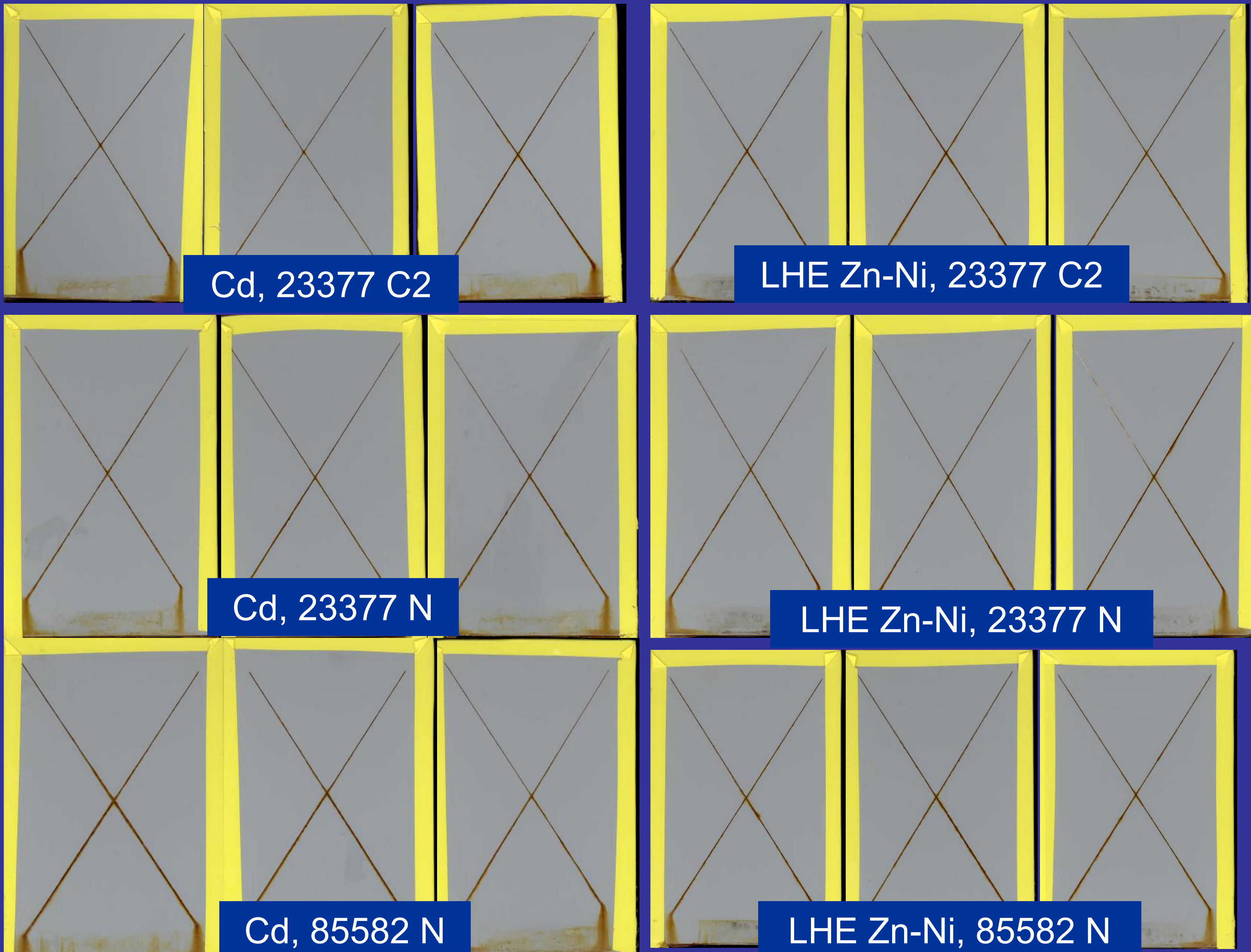
Sputtered Al, Scribed – 500 h

IVD-Al, Scribed – 500 h

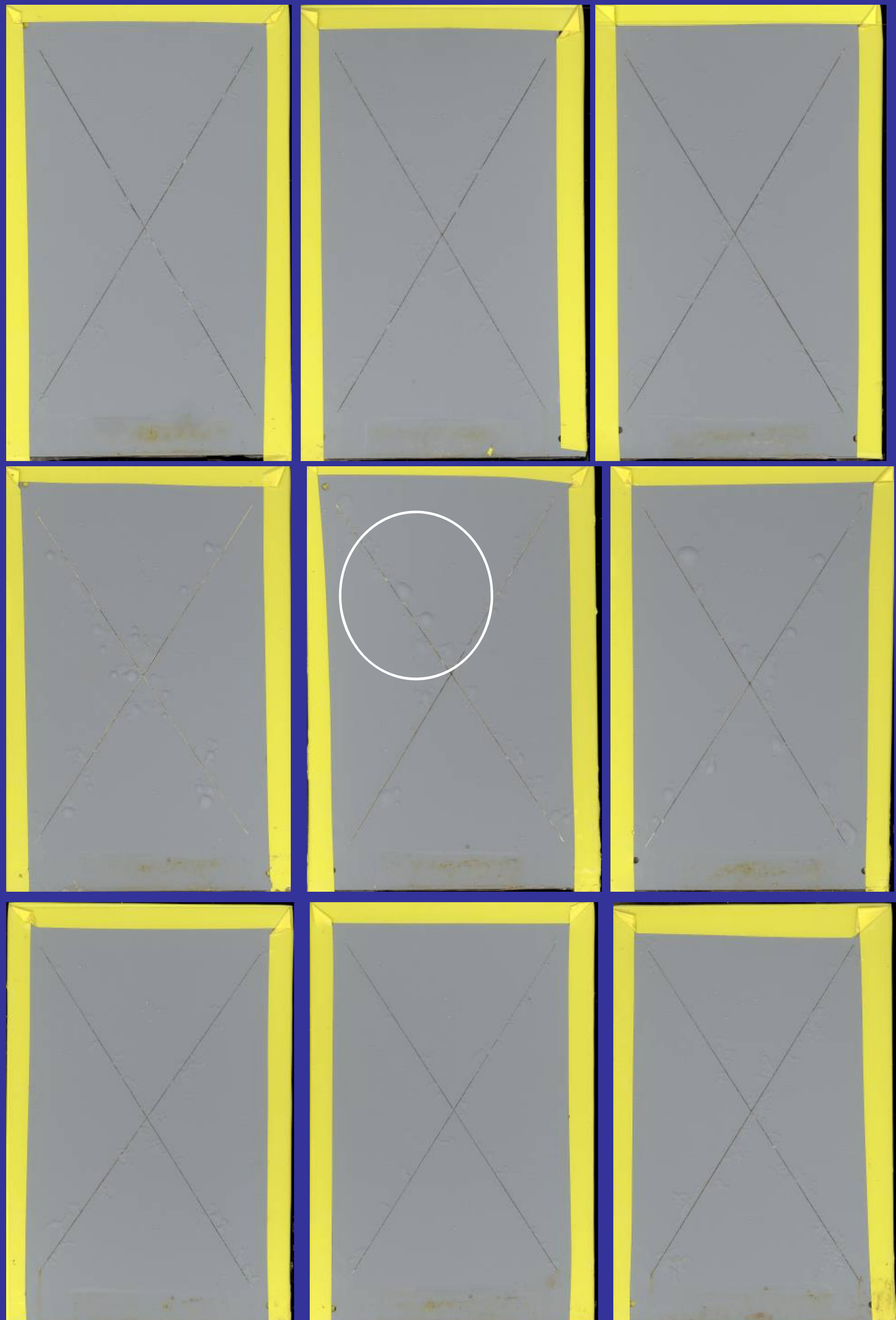
Graphical Representation of Bare, Unscribed Test Panel Ratings



Primed & Painted SO_2 Salt Fog,1000 h



Alumiplate - 1000 h

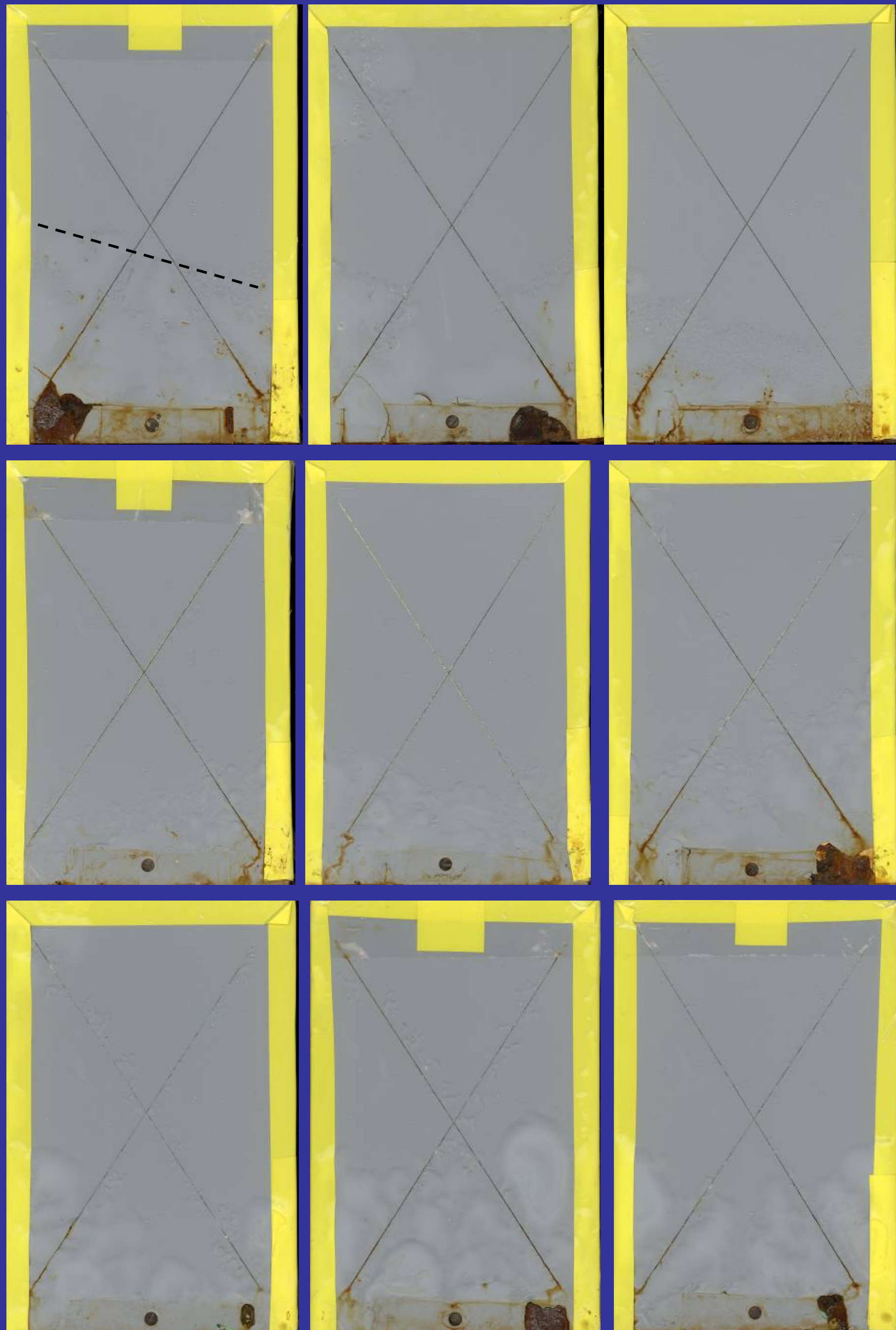


23377 C2

23377 N

85582 N

Sputtered Al – 840 h

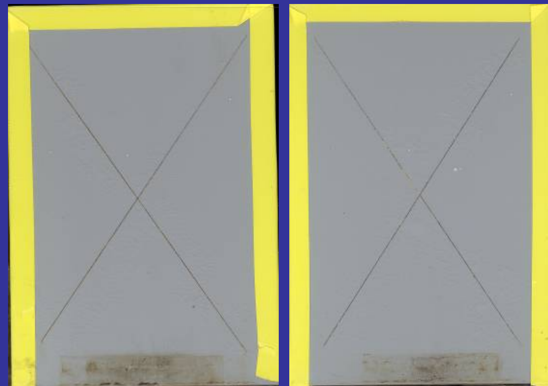


23377 C2

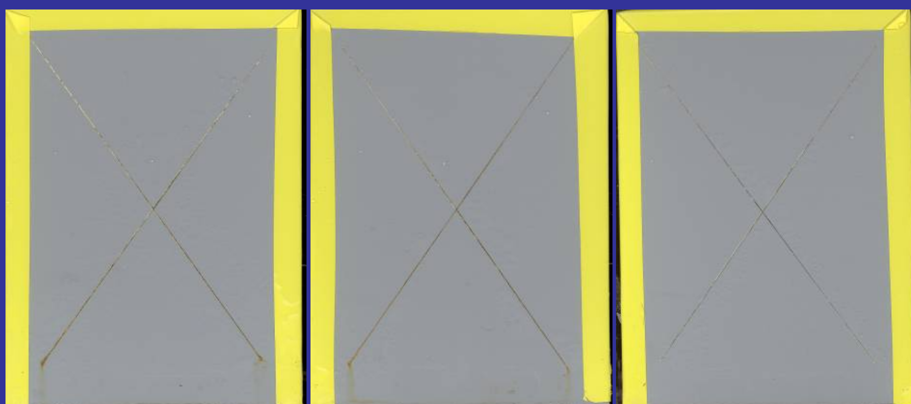
23377 N

85582 N

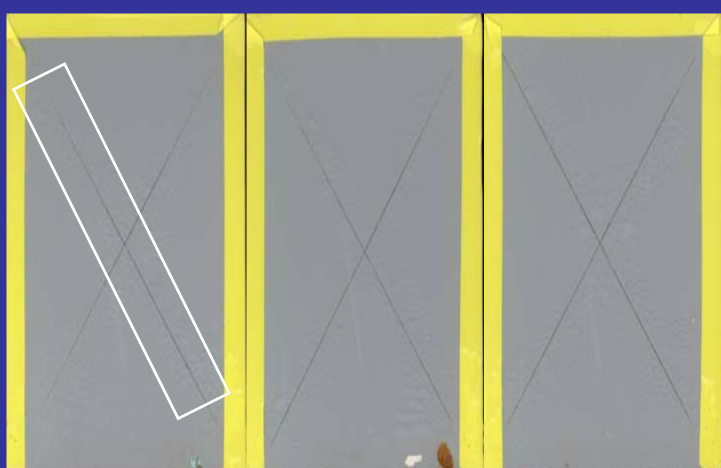
IVD-Al – 500+ h



23377 C2

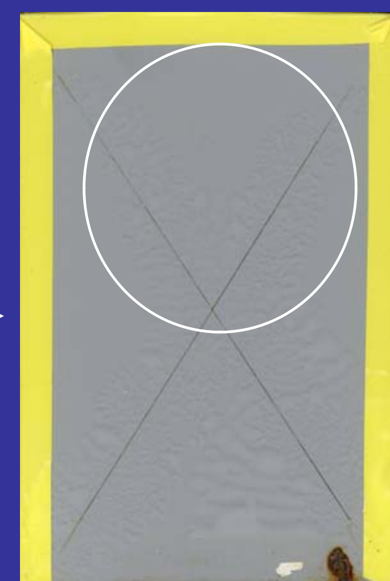


23377 N



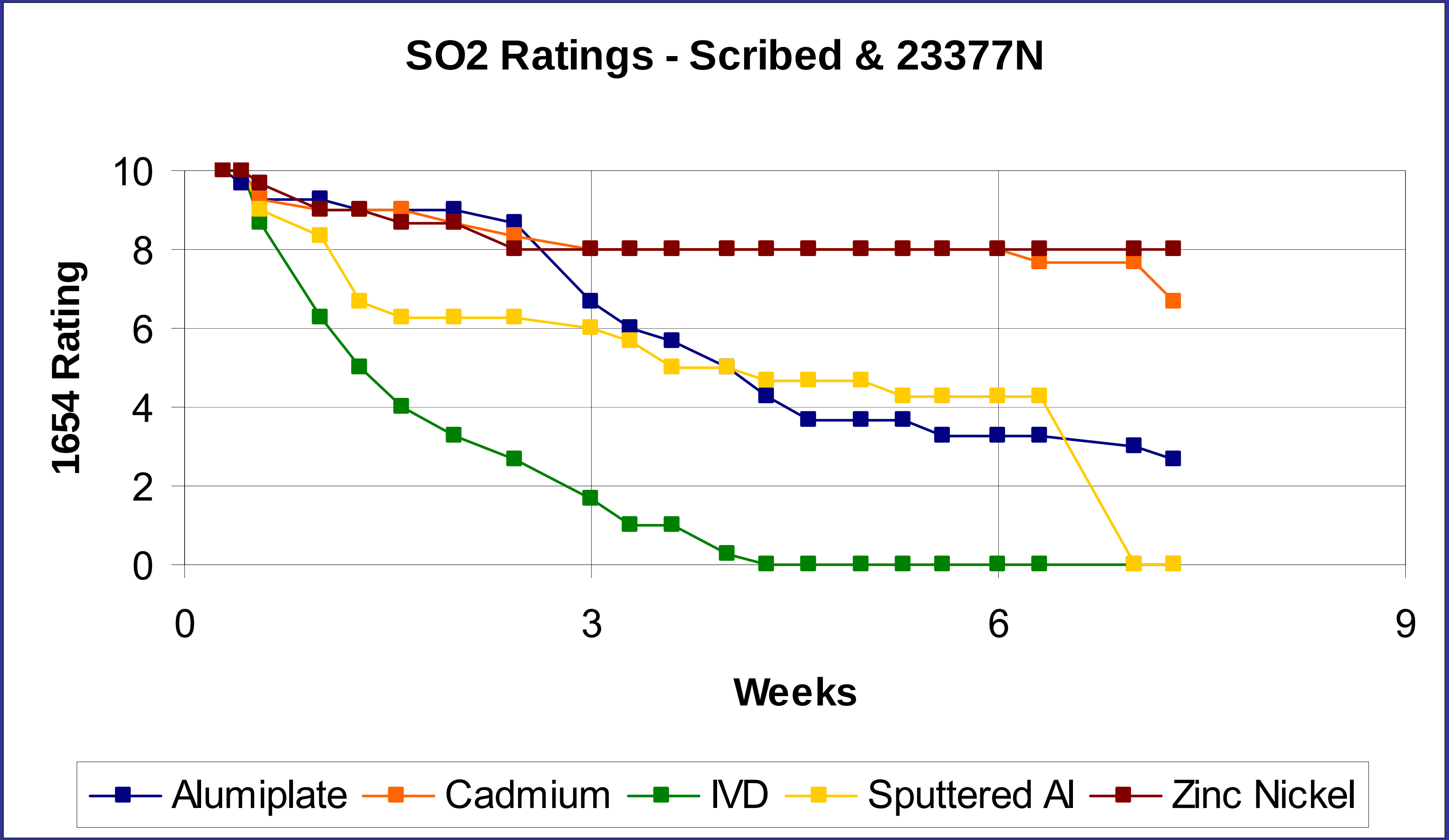
85582 N, 840 hrs;

1000 h



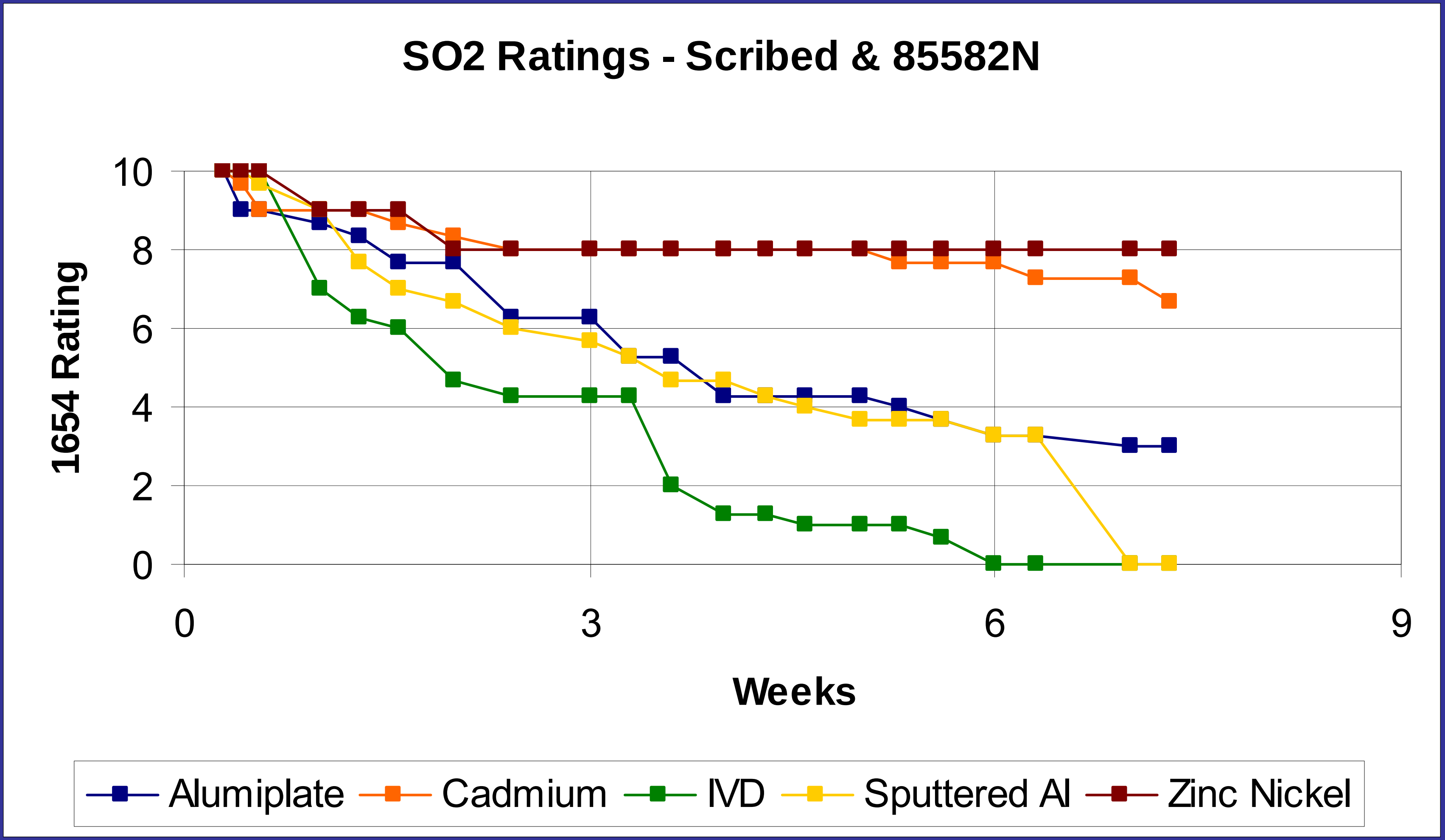
- Graphical Representation of Results, weekly through test (ASTM G 85.A4)

23377 Class N

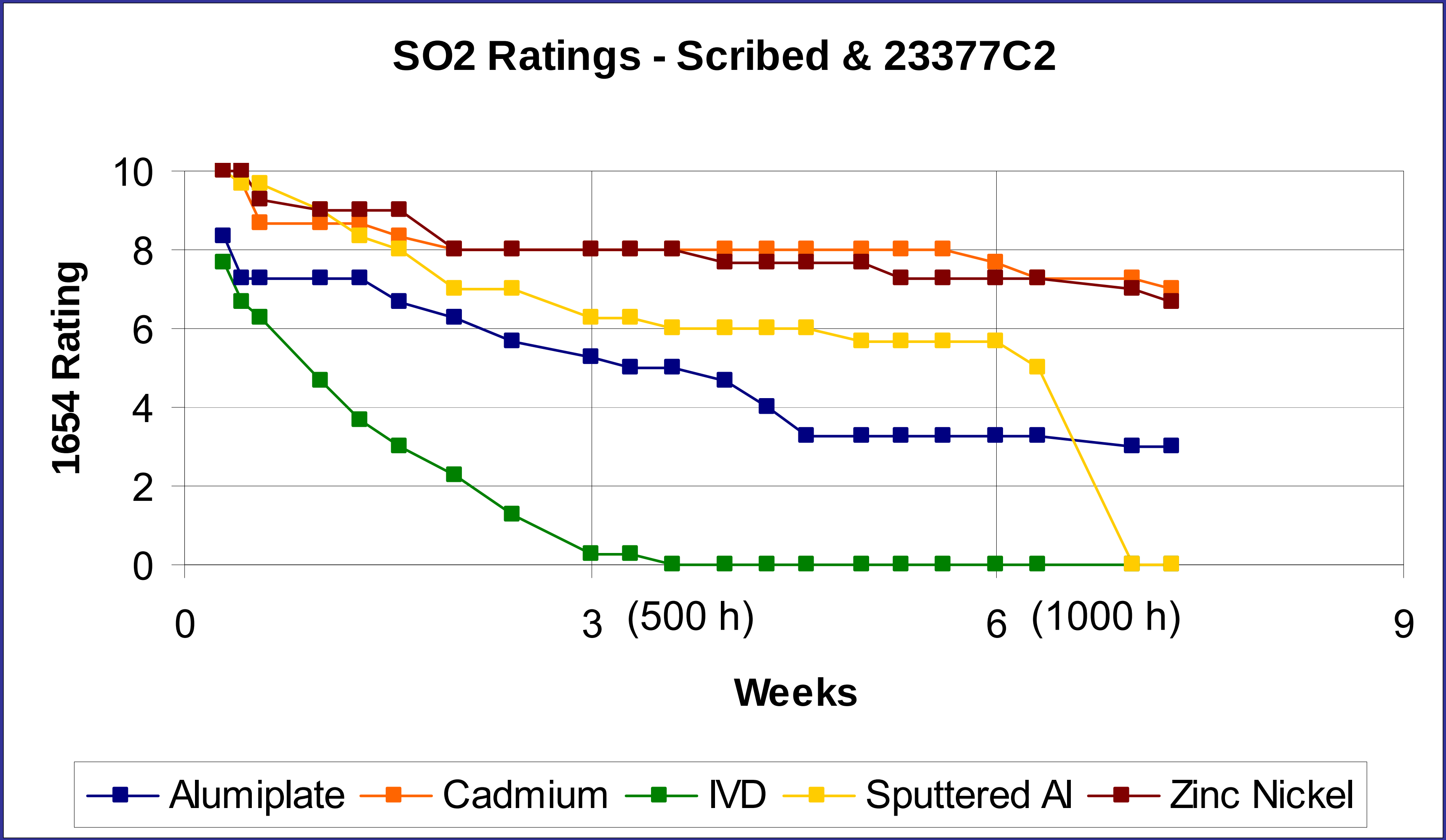


1. Cadmium and LHE Zn-Ni were approximately equivalent in scribe ratings with all three tested primers (red rust contained to scribe);

85582 Class N



23377 Class C2



- Overview of Cd Alternatives Test Performance
  - Residual Stress (Coating)
  - Residual Stress / layer thickness (Substrate)
  - Air Fatigue
  - Corrosion Fatigue
  - SCC
  - Acidic Salt Fog

Cd Alternative Coating Corrosion Performance Overview (4340 Steel)*

Coating	Thickness (mil), on SCC bars	Residual Stress (ksi) COATING	Residual Stress (ksi) Substrate	R.S. Layer Thickness (mil) Substrate	Open Circuit Potential (V)
Electroplated Al	2.20	+3.0	-113.2	4.57	-0.75
IVD-Al	0.50	-8.8	-79.6	2.17	-0.74
Cd	0.35	-3.2	-97.7	2.28	-0.76
LHE Zn-Ni	0.50	-3.6	-55.8	3.82	-0.75
Zn-6Ni	0.63	+46.3	-89.5	1.42	-1.00
	B.E.I.	X.R.D.			

* Source: NACE Tri-Service, Dec. ’07, P1792.

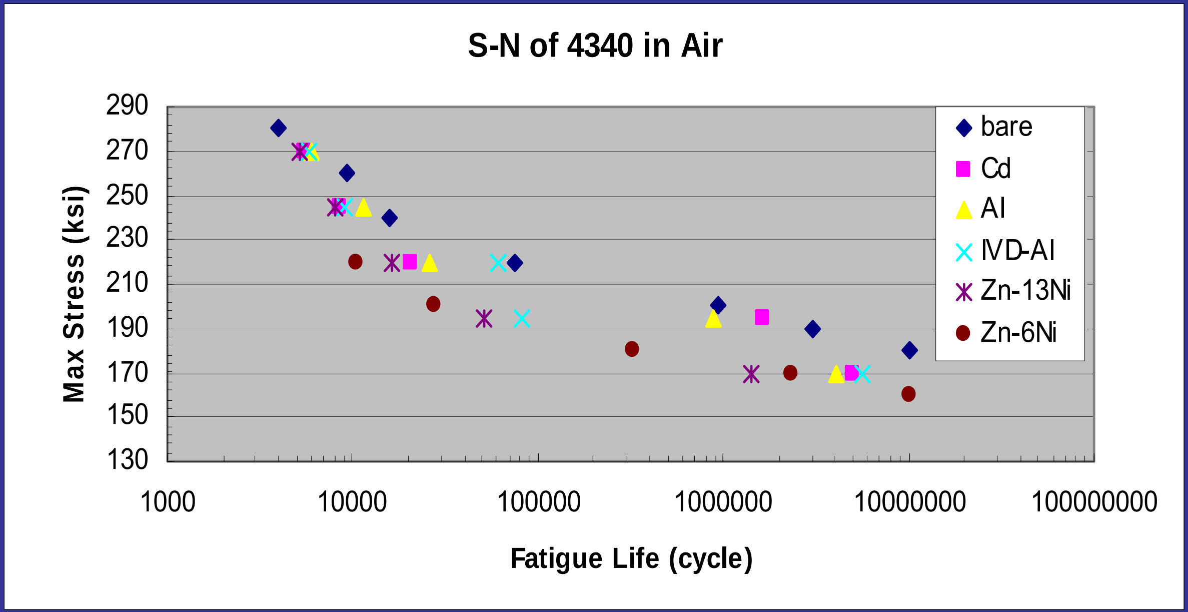
Cd Alternative Coating Corrosion Performance on 4340 Steel*

Coating	Stress Corrosion Cracking (Koscc)	SCC Ranking	Air Fatigue Ranking	Corrosion Fatigue Ranking	Acid SO2 Salt Fog, ASTM G85.A4
Sputtered Al	Not Tested	---	---	---	≥IVD
Electroplated Al	101.0	Best	Best	Best	Best (bare)
IVD-Al	52.7	Comparable to Cd	Best	Best	Least among Al coatings
Cd	49.5	CONTROL	CONTROL	CONTROL	CONTROL
LHE Zn-Ni	56.2	> Cd	Debit	Debit	> Cd (bare); Comparable (painted)
Zn-6Ni	36.8	OK (less data)	Debit	Debit	---
Method→	RSL Method		ASTM E 466; R=0.1; f=10/s	ASTM E 466; R=0.1; f=10/s	ASTM G85.A4

* Source: NACE Dec. ’07, P1792.

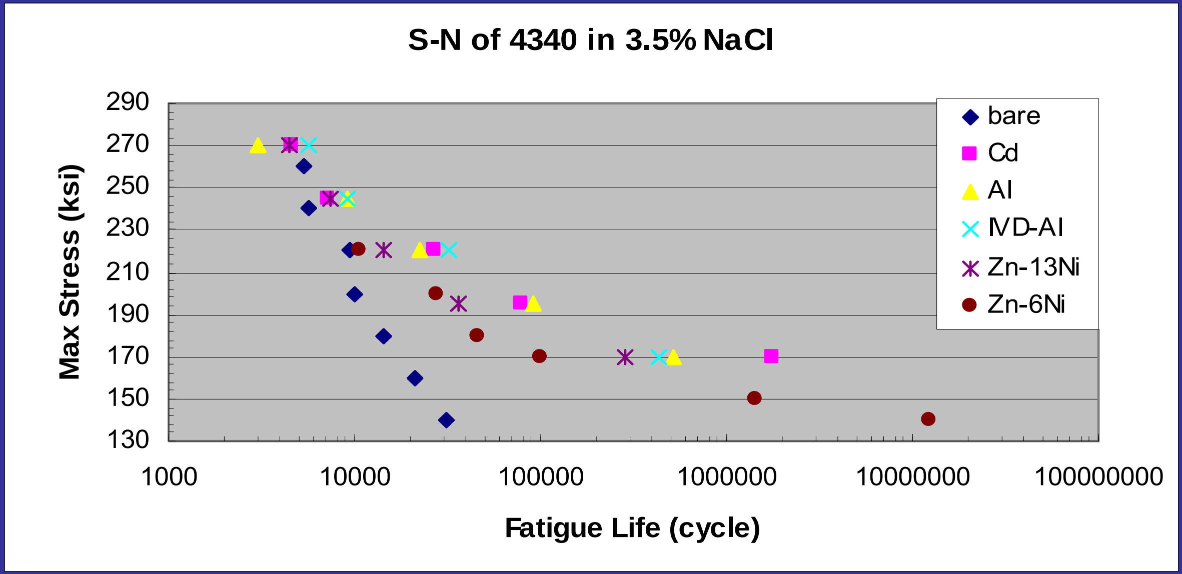
Air

(a)



3.5% NaCl

(b)



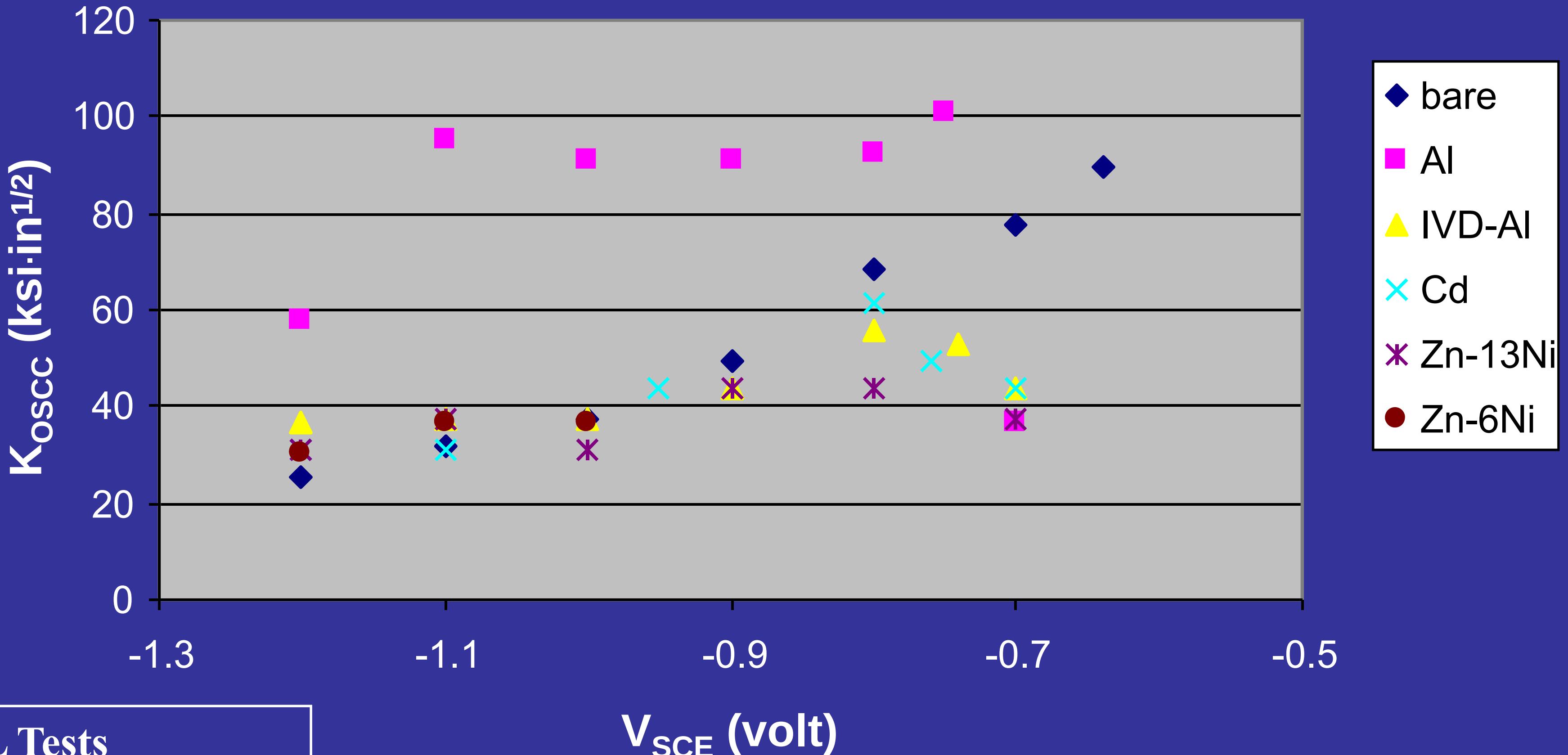
ASTM E 466 Fatigue Test Protocol;

R = 0.1

F = 10 Hz

Comparison of Fatigue Lives of Bare and Coated Specimens in (a) Air; and (b) 3.5% NaCl Solution

Stress Corrosion Cracking – Rising Step Load Tests (Coated vs. Bare 4340)



RSL Tests w/notched square bar specimens

Variation of K_{OSCC} with V_{SCE} for Bare and Coated Specimens

Conclusions

- Coatings induced substrate compressive stress states of varying degrees
  - Zn-6Ni and Alumiplate retained tensile stress in coating
- Sacrificial coatings reduce inherent fatigue resistance of 4340 in air, but largely preserve that value in 3.5% NaCl
- Al-based coatings performed best in:
  - Air & Corrosion Fatigue, bare SO_2, SCC (Alumiplate)
  - Thickness dependence of SCC results not characterized
- LHE Zn-Ni appears to have some fatigue advantage over Zn-6Ni; SO_2 results comparable or better than Cd (painted and bare, respectively); process advantages
- A more complete comparison of these Cd Alts includes Phase II tests nearing completion at ARL: (1) GM9540; (2) B 117, Galvanic, ...

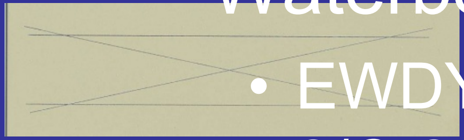
Non-Chromate Primer Demonstration

- Phase I
  - Qualification testing
  - Enhanced requirement testing (3000^{+}h ASTM B 117, ASTM G 85, D 3359…)
- Phase II
  - Primer down-select testing; review beach exposure data
  - Vendor Reformulation Validation
  - Depot Validation
- Field demonstrations

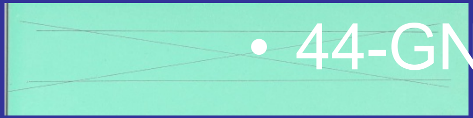
Paint hanger for North Island demonstrations.

Primer Candidates

- Primer downselection:
  - Waterborne MIL-PRF-85582 primer options:



    - EWDY048- Good beach results (5 yrs); Ltd. use on E-2/C-2; possible T-45 transition (2 yr demo).

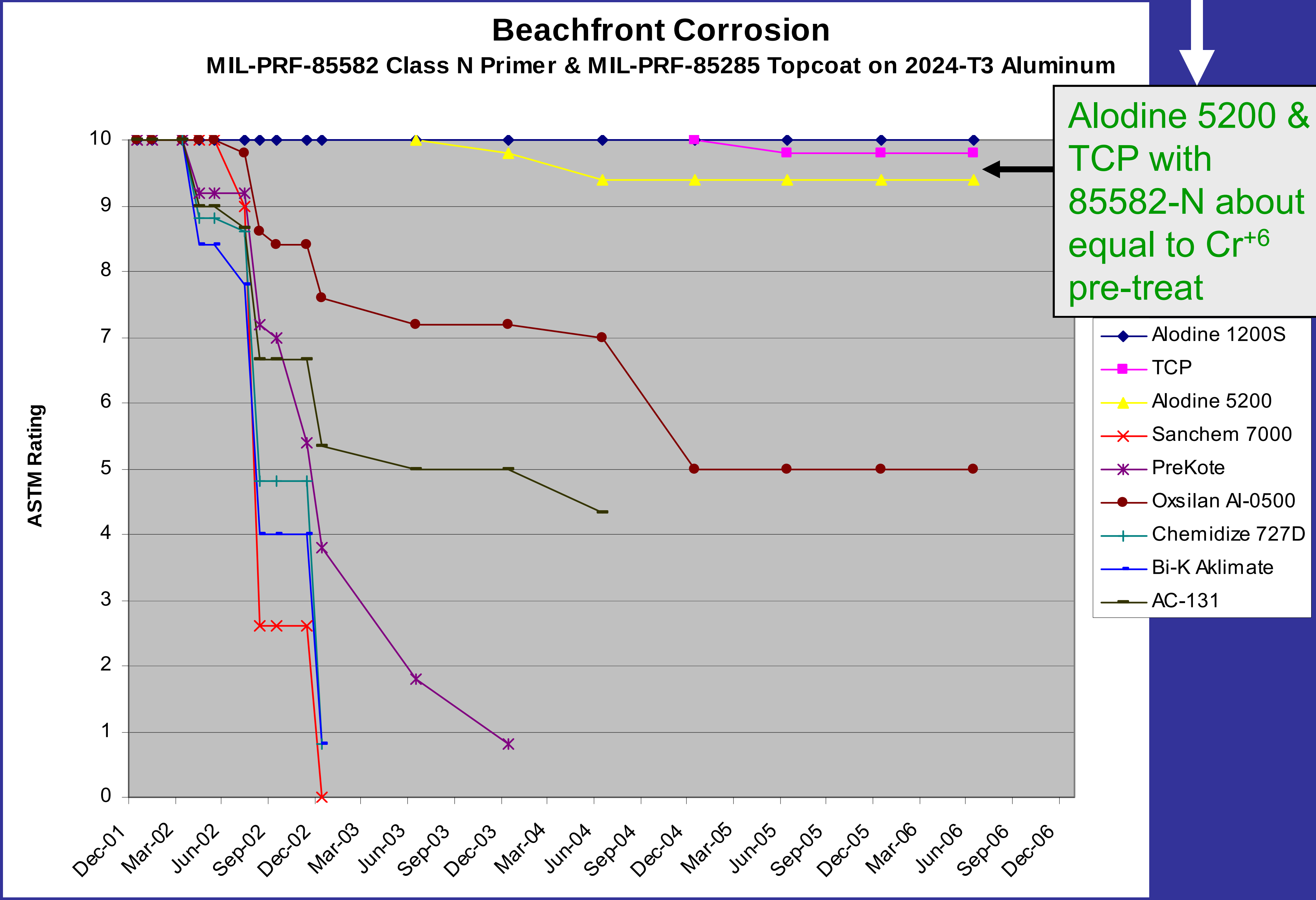


    - 44-GN-098
  - Solvent borne MIL-PRF-23377 primer options:

    - 16708TEP—Army helo demonstrations (2 yr)

    - 02-GN-083

    - 02-GN-084
    - Mg-rich Primer Efforts



Alodine 5200 & TCP with 85582-N about equal to Cr^{+6} pre-treat

4.5 year Beach Data (NCAP Project), Matzdorf & Nickerson

Depot validation


E-2/C-2 platform demonstration

- NAS North Island
  - 3 Primers Selected
    - PPG 85582-N (EWDY048) – Control
  - Painters to conduct sprayouts on practice a/c sections for (a) sprayability, (b) thickness control, (c) pot life… Evaluation datasheets
  - Using std hex chrome pretreatment
- FRC-SW (JAX)
  - Limited P-3 demo, several primers (wheel)

Acknowledgments

- NESDI (Naval Environmental Sustainability Development to Integration Program)
  - Fatigue, SCC, Residual Stress, G85
- ESTCP
  - Continuing support of Joint Cad Alts
- JG-PP
  - Demonstration setup (Cd Alts / LHE Zn-Ni), Cost-Benefit Analysis (through CTC); Non-Cr primer dem/val & test efforts

- FURTHER QUESTIONS ?

BACKUP SLIDES

Experimental Procedure

- Substrate Material & Specimen
  - Substrate Material: 4340 Steel Plate (3.8x15x30 cm)
  - Specimen: Round Tension Specimen, Round Hourglass Fatigue Specimen, Square Bar SCC Specimen with Center V-Notch of 60^o
- Coating: Polished Specimens were
  - Electrocoated with Al, Cd, Zn-6Ni & Zn-13Ni
  - Vacuum-Coated with IVD Al
- Coating Thickness, Chemical Composition & Residual Stress Determination
- Tension & Fatigue Tests
- Open Circuit Potential Measurement
- SCC Test: Accelerated SCC Test, Using Rising Step Load Test System, K_{OSCC} & K_{ISCC} Determination

Tension & Fatigue Tests

- Interlaken of 90 KN (20 kip) Capacity for Tension & Fatigue Tests
- Tension Test in Air, following ASTM E8
- Fatigue Test at R = 0.1 & f = 10 Hz in Air & 3.5% NaCl Solution of pH 7.3 under Load Control, following ASTM E466

OCP Measurement

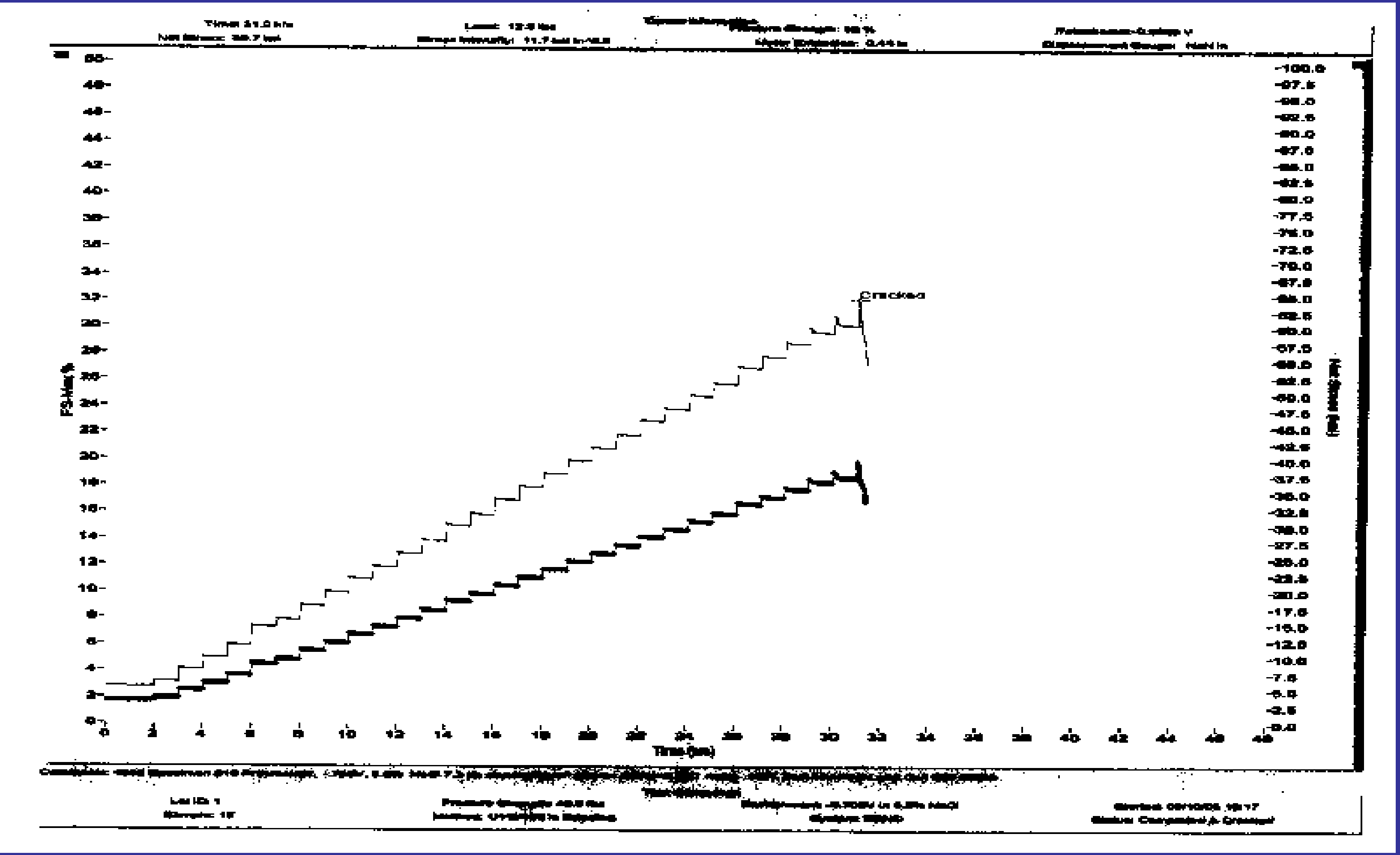
* Open Circuit Potential (OCP): Electrochemical Parameter of Corrosion Resistance, Measurable in Corrosion Cell
* OCP Cell, consisting of Specimen Electrode & Reference Electrode (SCE) in 3.5% NaCl Solution of pH 7.3
* Specimen Electrode: Flat Sheet of 38 x 7 x 1 mm, Bare & Coated
* Electrode Potential, Stabilized in 24 Hours, Taken as OCP

SCC Test

* Accelerated SCC Test in Rising Step Load (RSL) System
* RSL System, consisting of Bending Frame, Electrolyte Reservoir, Circulation Pump, Reference Electrode (SCE), Pt Counter Electrode, Computer & Printer
* Specimens: Bare (Unprecracked & Precracked) & Coated (Unprecracked)
* Loading: Step Loading in Four Point Bending at a Given Potential
* Load Drop: Indication of Threshold SCC, Calculation of Threshold Stress Intensity for SCC (K_{OSCC} & K_{ISCC})


Engineered Tough For Better Performance
Sontara AC

Sketch of Rising Step Loading



(* Load Drop: Threshold Stress Intensity for SCC, K_{OSCC} & K_{ISCC})

Threshold Stress Intensity for SCC
K_{OSCC} or K_{ISCC}

$$K_{OSCC} \text{ or } K_{ISCC} = \sigma \sqrt{\pi a} * F(a/W)$$

where

σ = gross stress = $6M/bW^2$

M = bending moment = Px

P = applied load

x = moment arm length

b = specimen thickness

W = specimen width

a = notch depth or crack length

F(a/W) : correction function

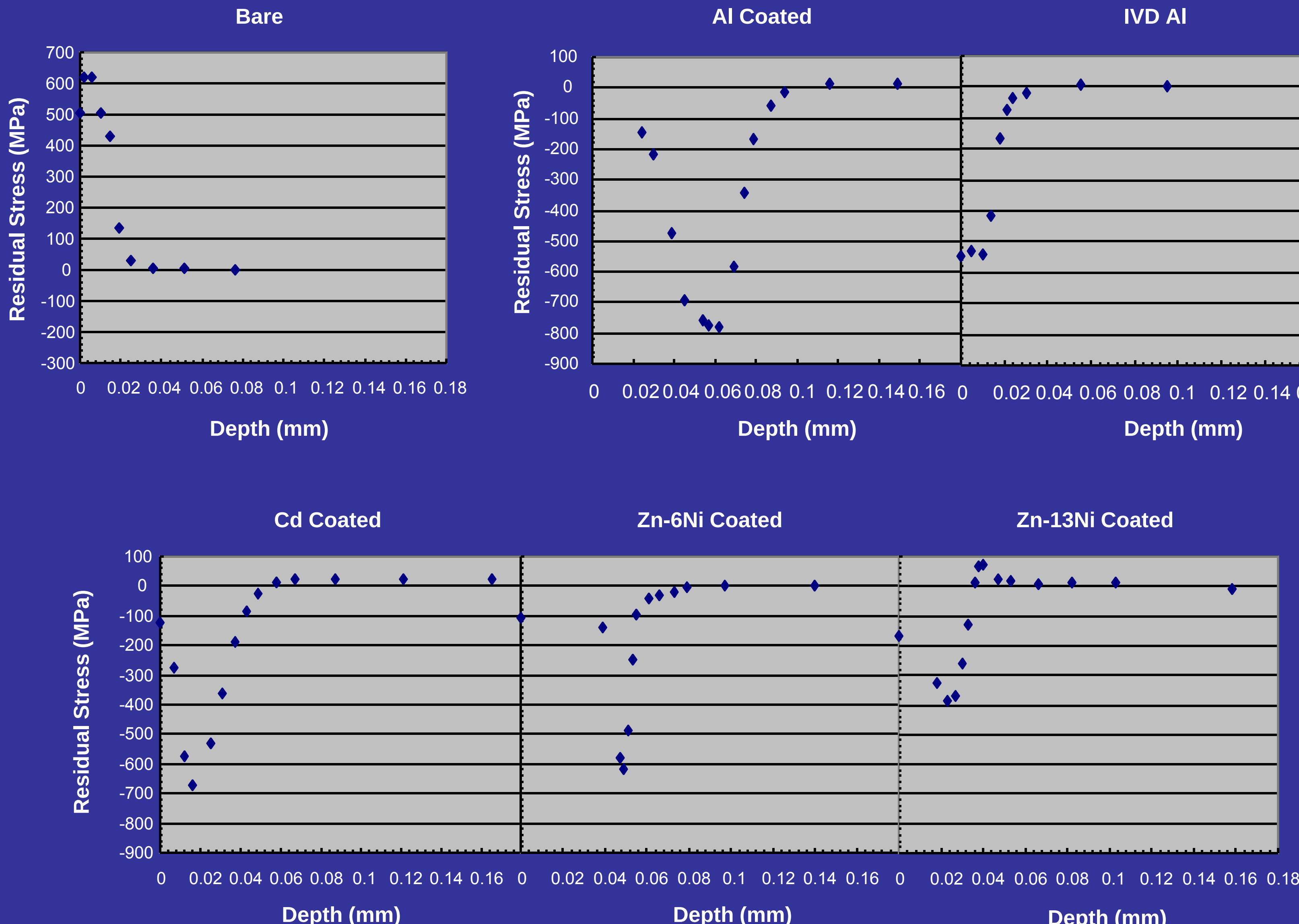
$$= 1.122 - 1.40(a/W) + 7.33(a/W)^2 - 12.08(a/W)^3 + 14.0(a/W)^4$$

Coating Composition (wt %)

Coating	Al	Cr	Fe	Ni	Zn	Cd	Total
Electrocoated Al	99.83	0.00	0.16	0.00	0.00	0.01	100.00
IVD Al	99.21	0.04	0.66	0.02	0.07	0.00	100.00
Cd	0.00	0.02	0.52	0.00	0.04	99.43	100.00
Zn-6Ni	0.02	0.03	1.30	6.42	92.23	0.00	100.00
Zn-13Ni	0.01	0.00	1.12	12.61	86.24	0.03	100.00

Residual Stress in Coating

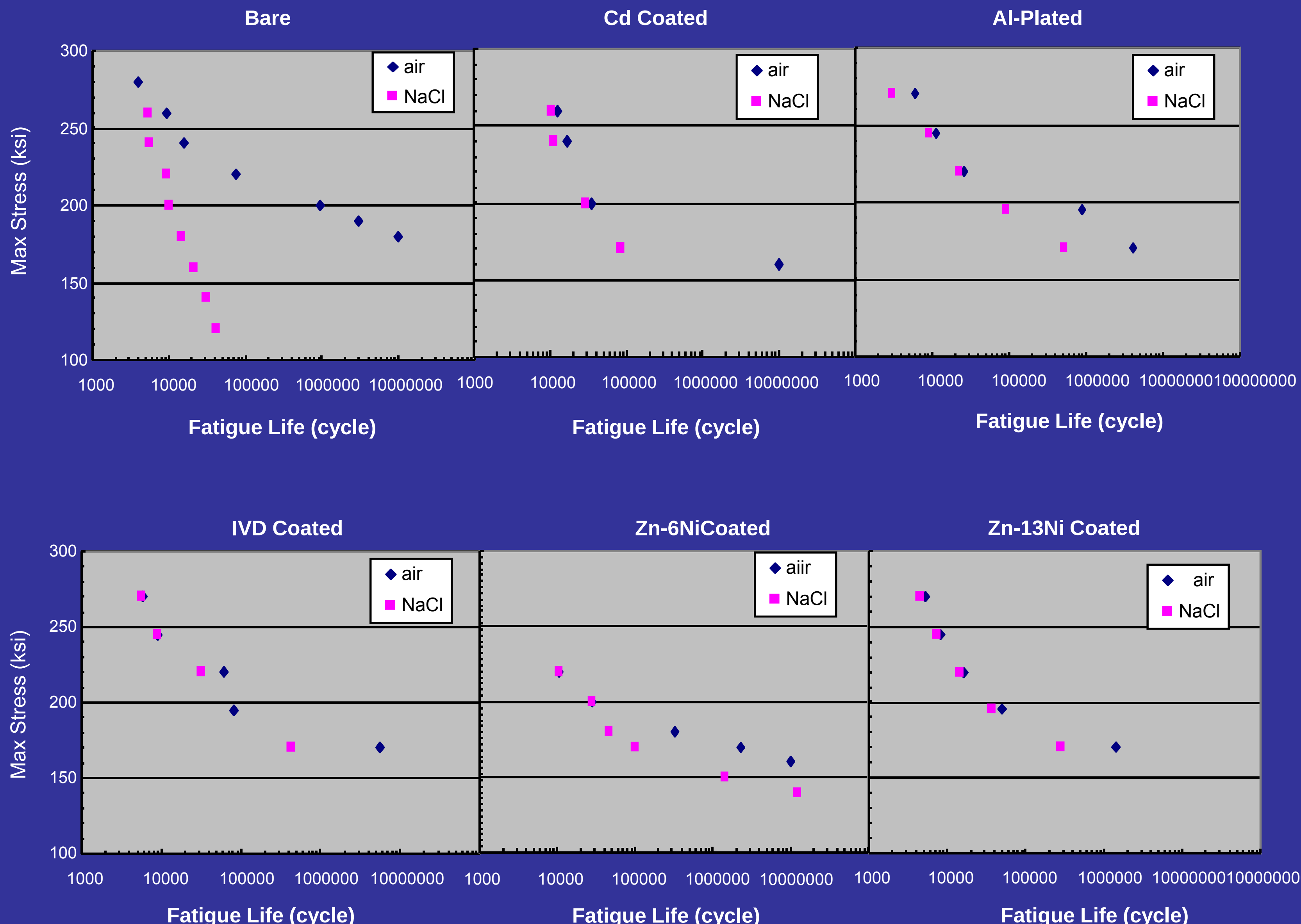
Coating	Residual Stress, MPa (ksi)
Electrocoated Al	+ 21 (+ 3.0)
IVD Al	- 61 (- 8.8)
Cd	- 22 (- 3.2)
Zn-6Ni	+ 319 (+ 46.3)
Zn-13Ni	- 25 (-3.6)



Residual Stress in Substrate

Residual Stress in Substrate

Coating	Peak Residual Stress Magnitude, MPa (ksi)	Peak Residual Stress Depth, mm (mil)	Residual Stress Layer Thickness, mm (mil)
Bare	+ 621 (+ 90.0)	0.006 (0.24)	0.076 (2.99)
Electro Al	- 781 (- 113.2)	0.062 (2.44)	0.116 (4.57)
IVD Al	- 549 (- 79.6)	0 (0)	0.055 (2.17)
Cd	- 674 (- 97.7)	0.016 (0.63)	0.058 (2.28)
Zn-6Ni	- 617 (- 89.5)	0.049 (1.93)	0.097 (3.82)
Zn-13Ni	- 385 (-55.8)	0.023 (0.91)	0.036 (1,42)

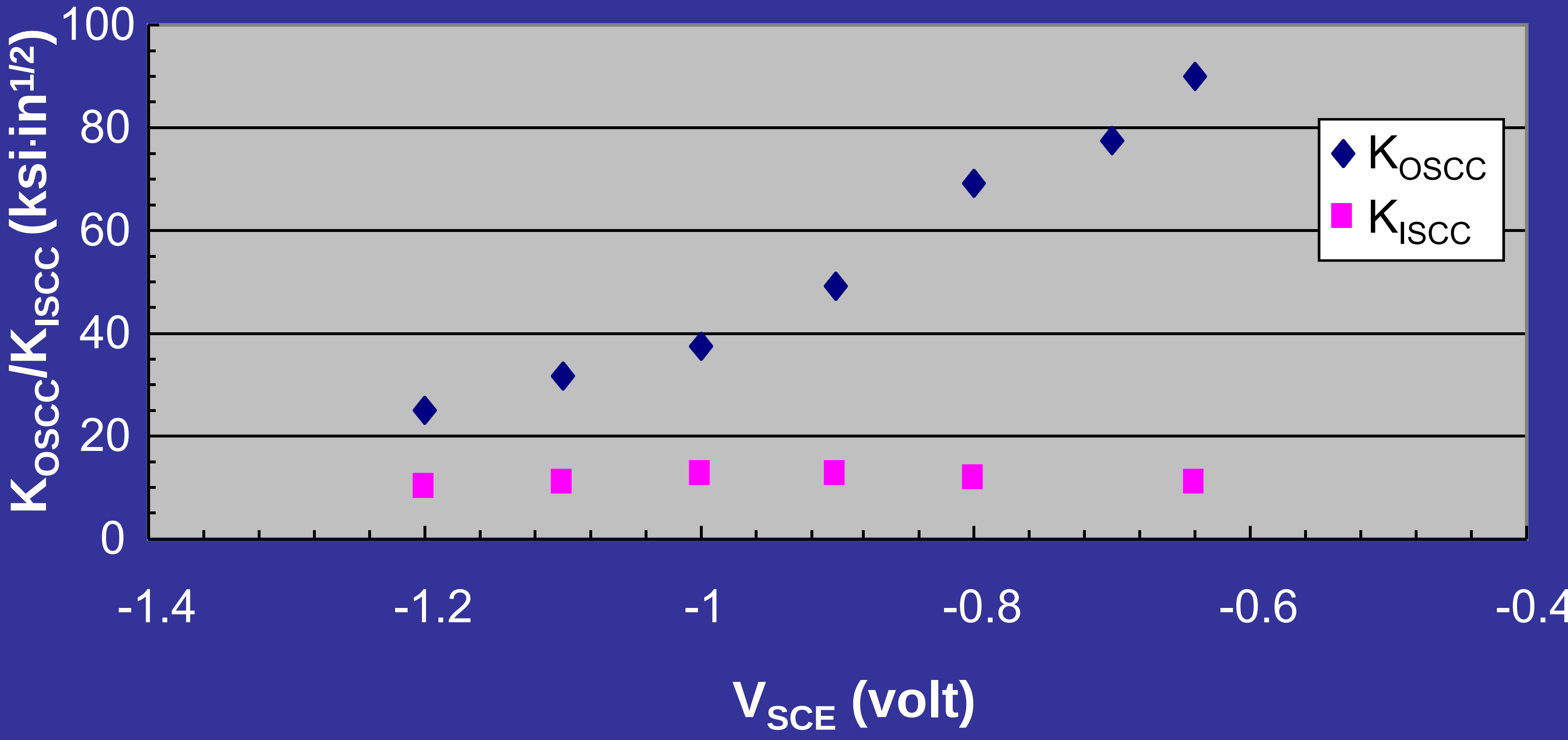


Stress-Life Curves of Bare and Coated Specimens in Air and 3.5% NaCl Solution

Open Circuit Potential OCP & Threshold Stress Intensity for SCC K_{OSCC}

Coating	OCP (volt)	K_{OSCC} MPa$\sqrt{m}$	K_{OSCC} ksi$\sqrt{in}$
Bare	- 0.64	98.5	89.6
Electrocoated Al	- 0.75	111.0	101.0
IVD Al	- 0.74	57.9	52.7
Cd	- 0.76	54.4	49.5
Zn-6Ni	- 1.00	40.4	36.8
Zn-13Ni	- 0.75	61.8	56.2

K_{OSCC} & K_{ISCC} (4340 Bare)



Variation of Threshold Stress Intensity for Stress Corrosion Cracking in As-Machined (Un-precracked) and Precracked Bare Specimens, K_{OSCC} and K_{ISCC}, with Applied Electric Potential V_{SCE} {At OCP = - 0.64 volt, K_{OSCC} = 98.5 MPa$\sqrt{}$m (89.6 ksi$\sqrt{}$in) & K_{ISCC} = 11.5 MPa$\sqrt{}$m (10.5 ksi$\sqrt{}$in)}

Discussion

- Residual Stress
- Fatigue
- SCC

Residual Stress

- Residual Stress in Structural Components
  - Beneficial, if Compressive
  - Detrimental, if Tensile

- Residual Stress in Coated Components Generated by:
  - Lattice Distortion due to Its Misfit at Interface between Coating & Substrate
  - Coating Condition & Bath Composition

Residual Stress in Bare Specimen

* Residual Stress Determined:Tensile
* Specimen Prepared by EDM and Hand Polishing with Emery Cloth
* EDM, involving Electric Sparking, Thin Layer Melting, Cooling, Solidification & Shrinkage, inducing Tensile Residual Stress
* Hand Polishing, inducing Compressive Residual Stress
* Residual Stress by EDM > Residual Stress by Hand Polishing

Lattice Parameters of Coating & Substrate

Element	Crystal Structure	Lattice Parameter (Angstrom)
Al	fcc	a = 4.0491
Cd	hcp	a = 2.9787, c = 5.6173
Zn	hcp	a = 2.6649, c = 4.9470
Fe-C, Martensite (0.4% C)	bct	a = 2.8530, c = 2.9060

Residual Stress (RS) in Coating

* Lattice Parameter of Cd > Lattice Parameter of Martensite, and RS: Compressive in Cd Coating
* Lattice Parameter of Al > Lattice Parameter of Martensite, but RS: Tensile in Electro Al & Compressive in IVD Al
* Lattice Parameter of Zn > Lattice Parameter of Martensite, but RS: Tensile in Zn-6Ni & Compressive in Zn-13Ni

UTS of Coating & Substrate

Material	UTS, MPa (ksi)
Al	40 – 70 (6.5 – 10.2)
Cd	69 – 83 (10.0 – 12.0)
Zn	283 – 324 (41.0 – 47.0)
Ni	317 (46.0)
4340	1,964 (284.8)

[* UTS proportional to Fatigue Strength]

Open Circuit Potential OCP & Threshold Stress Intensity for SCC K_{OSCC}

Coating	OCP (volt)	K_{OSCC} MPa√m	K_{OSCC} ksi√in
Bare	- 0.64	98.5	89.6
Electrocoated Al	- 0.75	111.0	101.0
IVD Al	- 0.74	57.9	52.7
Cd	- 0.76	54.4	49.5
Zn-6Ni	- 1.00	40.4	36.8
Zn-13Ni	- 0.75	61.8	56.2